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RESONANT SCATTERING STATE OF THE NEGATIVE HYDROGEN MOLECULE ION.

Resonant Scattering State of the Negative Hydrogen Molecule Ion.[+]

by

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Abstract

An ab-initio calculation is made on a resonant state of the H_2^- ion by an approximate variation method. Excellent agreement with experiment is obtained. Physical justification is given for the use of the approximate variation method.

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I. Discussion

Several recent experiments have shown features that indicate the presence of an H_2^- ion. Schultz[1] proposed a state of H_2^- in the formation of H and H^- by electron impact on hydrogen gas. Khvostenko and Dukel'shii[2a] proposed a similar mechanism in electron impact measurements on H_2, i.e., $H_2 + e \longrightarrow (H_2^-) \longrightarrow H + H^-$. They also detected a negative ion of mass two by mass spectrometer[2b] upon bombarding a mixture of water and antimony gas with electrons. In ref. (2b) is explained why this was felt to be H_2^- with a lifetime long enough to be observed, rather than the other possibility, D^-. In astrophysics[3] it has been suggested that H_2^- occurs in the solar corona and dissociates into H and H^-.

The latest of these have been some electron scattering experiments by Simpson and Kuyatt,[4,5] where a highly monochromatic electron beam was scattered off hydrogen gas. A plot of current vs. energy was made, and resonances corresponding to a set of vibrational levels were observed. From these levels the spectroscopic constants ω_e, $\omega_e x_e$, and the approximate E_0 were calculated. The spectroscopic constants are very similar to those of H_2, $^1\Pi_u$ or $^3\Pi_u$, however the threshold energy was lower than both, thereby suggesting the possibility of a resonant state of H_2^- consisting roughly of an inner σ electron and two outer electrons, with symmetry $^2\Sigma_g$.* (Note that the outermost, planetary electron would not greatly affect the field in which the nuclei move.)

The predominant common feature of all these experiments is that they are of a scattering nature, and thus the observations could be of a real bound excited state, or of a resonance in the continuum.

Previous papers concerning theoretical calculations[6] on H_2^- show that there is no bound state with an energy lower than that of the H_2 X $^1\Sigma_g$ state of the hydrogen molecule with an electron at infinity. In the computations of (6) many configurations were tried, with complete variation of non-linear and linear parameters, and in all cases the variation method itself produced the equivalent of a hydrogen molecule with an electron in the continuum.

Thus it was decided to look for a bound state of a different nature, i.e., following the suggestions of experiment, a state with one inner σ electron and two outer π electrons, such that essentially the wave function would resemble the trapping of an electron in a π orbital by a $^1\Pi_u$ or $^3\Pi_u$ hydrogen molecule. This appears physically resonable since an incoming electron would "see" a σ electron about two nuclei, and a 1π electron perpendicular to it, or therefore,

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* Σ^+ and Σ^- are essentially degenerate for this discussion. This can be seen from the small overlap of the (ξ,η) parts of 1π and 3π.

a net attractive charge which was greater than zero, since the excited orthogonal outer electron would not screen for the incoming one. Also, in both the two electron ($1\sigma\ 1\pi$) and the three electron ($1\sigma\ 1\pi\ 3\pi$) systems, the electrons are highly uncorrelated. The importance of this will be discussed later.

Note the difference between this and electron capture by a hydrogen atom to form H^-. In atoms an incoming electron can induce polarization, but in the hydrogen molecule, most of the electron density must remain between the two nuclei to form the bond, and therefore cannot be polarized nearly as much as two separate atoms by the incoming electron. This gives another physical picture of the reason a state like the ${}^1\Sigma_g$ state of hydrogen cannot capture an electron, but states like ${}^1\Pi_u$ and ${}^3\Pi_u$ might be likely to.

Use of a trial variation function of this type could lead to two possible results. First, but highly unlikely due to experimental evidence and previous theoretical calculations, there could be a true bound state which would be a solution to the Schroedinger equation, with a true variation principle and an energy less than that of the ground state of the hydrogen molecule. Or secondly, the $1\sigma\ 1\pi$ configuration could cause a narrow, but very deep potential well for the incoming electron, such that there is a resonance, composed of a highly localized, relatively long-lived combination of continuum states (wave packet).

The problem then is to construct such a highly localized wave packet from continuum functions having a lifetime long enough to be observable in other words, with a low probability of a radiationless transition from the resonant state to the hydrogen molecule plus an electron of proper energy in the continuum.

Using the physical arguments above, a configuration which will hopefully have a deep potential well for the scattered electron and a small overlap with the $H_2\ {}^1\Sigma_g$ + e must be constructed. A preliminary calculation was made with a trial function with configuration $1\sigma 1\pi 1\pi$. Even this rough calculation confirmed the suspicion that there is no bound discrete state with an energy less than that of $H_2\ {}^1\Sigma_g$ + e. The second possibility then becomes the one which must be investigated. Certain difficulties arise, for there is no longer a variation theorem and no rigorous minimum principle. How does one select the parameters of a wave packet and calculate the energy under these circumstances? Two arguments will be given to show the validity of an approximate variation principle. They are based on the fact that the system is to a large degree uncorrelated, with weak interactions between electrons, and that the deep potential causes a resonance packet, which is a function of time, and this time dependence may, to

a first approximation, be expressed in the parameters of the trial function. Neither of these arguments can be proven rigorously, but the subsequent discussion and results show them both to be physically quite valid.

The variation principle requires that all bound states be orthogonal to all lower energy states of the same symmetry. In the present case, the packet approximating a bound state must be orthogonal to all $^2\Sigma_g$ states of $H_2\ ^1\Sigma_g$ plus an electron at infinity. Although rigorous orthogonality is impossible since both states are $^2\Sigma_g$, effective orthogonality (zero overlap) is possible if the packet is constructed so the two inner electrons are $1\sigma_g 1\pi_u$, which is orthogonal to $H_2\ ^1\Sigma_g$. The variation is restricted such that the two inner electrons must remain $1\sigma_g 1\pi_u$, i.e., $H_2\ ^1\Pi_u$ and therefore are always orthogonal to $H_2\ ^1\Sigma_g$. Orthogonality is also expected because the continuum electron in the lower state overlaps negligibly with the localized $1\sigma_g 1\pi_u 3\pi_u$ packet. This has been verified by direct calculation of the overlap in a number of non-equal energy cases. If the packet were to overlap with any continuum state it would have to be those of equal energy. The following argument is presented to account for this case. It has been noticed in retrospect that good agreement with experiment, the insensitivity of the variation of one electron's parameters to the other's parameters, and the resulting well separated molecular orbitals indicate that the electron correlation is very small. If this is the case, $1/r_{12}$ can be considered as a perturbation and a zero order argument that the overlap is zero can be given. Higher order perturbation theory will give negligible overlap if there is "convergence" by zero order. If $\langle V_{corr.}\rangle$ is small then the configuration used is a product of three H_2^+ functions. The packet is $1\sigma_g 1\pi_u^{+1} 3\pi_u^{-1}$; the continuum is $1\sigma 1\pi_u^{+1}$ [illegible]π_u^{-1} and these are clearly orthogonal by the orthogonality of H_2^+ orbitals. Therefore by perturbation theory, weak correlation implies that a restricted variation (restricted to different H_2^+ orbitals) allows a true minimum principle with which to calculate the "best" energy. To verify this it is noted in Holøein, and [illegible] and Dahler's work on helium[7] very reasonable results are obtained when the variation principle is applied to such uncorrelated packet states as $(2p)^2\ ^3P_g$, $(2p)^2\ ^1S$, $(2p3p)\ ^1P_g$, $(2p3d)\ ^1D_u$, and $(2p3d)\ ^3D_u$. On the other hand Holøien finds that the $(2s)^2\ ^1S$ state[7b] in H^- has a lower energy than that of the $(1s)^2\ ^1S$ state of H^-. In helium, the reverse, expected result is found. It is felt by the authors that the result on H^- is in error because in the $(2s)^2\ ^1S$ case correlation is not small and no approximate variation principle holds. Clearly $(2s)^2$

being lower than $(1s)^2$ is unphysical and contrary to the more extensive calculation of Pekeris[8a] where he shows only one bound state exists. The $(2s)^2\ {}^1S$ problem in helium is also not completely settled.[8a,b] This is felt to be due to the correlated nature of the system and the consequent failure of the variation method.

Another justification of the variation principle is that since this is a resonance, the energy calculated by variation is not a discrete eigenvalue, but the average of a spread of energies. This average energy must be a function of time, since the packet must eventually spread. Now there is no explicit time dependence in the variation function, but the variable parameters regulate the spread of the wave packet, and thus the parameters themselves may be considered as time dependent and tending to cause the resonant wave packet to delocalize as time increases.

To achieve the longest lived resonant state in the restricted region of Hilbert space selected, therefore, by the uncertainty principle, ΔE_{av} must be minimized.

This can be stated as $\bar{E}_{av} = E_{av}(\alpha_i)$, where α_i are the variable parameters, and $\alpha_i = \alpha_i(t)$. Then to minimize ΔE,

$$\frac{\partial E_{av}}{\partial t} = 0 = \sum_i \frac{\partial E_{av}}{\partial \alpha_i}\frac{\partial \alpha_i}{\partial t} \qquad (I.1)$$

But the variation method causes $\partial E_{av}/\partial\alpha_i = 0$ for all α_i therefore minimizing ΔE_{av} and maximizing Δt. This in essence selects the best (longest lifetime) wave packet possible in the region of Hilbert space considered. Note that the variation alone will not give a long lifetime state, but will only give the packet of longest lifetime among the class chosen.

The use of the variation principle has now been physically justified. Thus the question becomes: is the state which has been found of long enough lifetime to be observed? An appeal to the ultimate agreement with experiment could be made, with the claim that the state clearly exists long enough to vibrate. However, it is preferable to give a physical argument based on the weakness of the correlations and the resulting perturbation method to indicate a long lifetime.

To demonstrate this, consider the standard auto-ionization picture of bound states in the continuum.[9] The argument will be outlined here for helium because it is easier; it will be clearly extendable to the H_2^- case. If

$1/r_{12} = V_{\text{corr.}}$ is small the zero order wave functions are products of two hydrogenic orbitals. The functions and levels fall into three classes with overlapping energies:

(a) $E = -\frac{1}{n_1^2} - \frac{1}{n_2^2}$ both one-electron functions bound

(b) $E = -\frac{1}{n_1^1} + \frac{k_2^2}{2}$ one one-electron function bound and one continuum

(c) $E = \frac{k_1^2}{2} + \frac{k_2^2}{2}$ both continuum

When n_1 and n_2 are large in (a) and n_1 small in (b), a k can be found such that $E_{\text{cont.}} = E_{\text{bd.}}$, i.e., there exists a bound state in the continuum. A non-radiative transition from the bound to continuum state of equal energy is given by the probability of auto-ionization (see ref. 9, and ref. 7a). Therefore the transition probability, w, is proportional to

$$\left| \left\langle \text{bound} \left| \frac{1}{r_{12}} \right| \text{cont.} \right\rangle \right|^2 \delta(E_{\text{bd.}} - E_{\text{cont.}})$$

The lifetime of the bound state is proportional to w^{-1}.

Now if the correlation is small, an assumption upon which the equation for w was derived, the first order correction to the bound state function due to correlation is given by

$$(H_0 - E_{\text{bd.}})\, \psi_1 + \left(\frac{1}{r_{12}} - E_1\right) \psi_{\text{bd.}} = 0$$

If ψ_1 is expanded as usual on all other states of the system, and substituted back into the perturbation equation, then multiplied by $\psi_{\text{cont.}}$ and integrated, the result is,*

$$\left\langle \text{bound} \left| \frac{1}{r_{12}} \right| \text{cont.} \right\rangle + C_{\substack{\text{bd. on}\\ \text{cont.}}} (E_{\text{bd.}} - E_{\text{cont.}}) = 0$$

Now when $E_{\text{bd.}} = E_{\text{cont.}}$ the matrix element is to first order zero and w is then of the form $x\delta(x)$, $x = E_{\text{bd.}} - E_{\text{cont.}}$, and therefore approximately zero. Higher order perturbation theory modifies this, but if the perturbation is really small, in a negligible way.

In support of this argument it is pointed out that the types of resonant states that have been observed are generally highly uncorrelated and ones in which the "resonant trapped" electron sees a deep well due to the rest of the system. It is exactly this type of state for which successful variation calculations have been carried out.

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* In this expression, the continuum normalization factors have been cancelled from both sides.

II. Wave Function and Calculation Methods

Using the physical arguments above, it was decided to use a one configuration three-electron variation function, having ${}^2\Sigma_g$ symmetry, such that loss of the outer electron would not be able to yield a ${}^1\Sigma_g$ state, but only a ${}^1\Pi_u$ state. The elliptic molecular orbitals and calculation methods of Harris and Taylor were used.[10]

For one configuration the variation function becomes:

$$\Psi^{d}(\bar{r},\bar{\sigma}) = 6^{-\frac{1}{2}} \sum_{j=1}^{2} \sum_{P} U_{jd}(P)\, \Phi(P\bar{r})\, \Theta^{3}_{\frac{1}{2}0j}(\bar{\sigma}) \qquad \text{(II.1)}$$

where $U_{jd}(P)$ is the jd element of the matrix representation of the permutation P on the spin eigenfunction bases. The Θ^{n}_{SMj} are:[11]

$$\Theta^{3}_{\frac{1}{2}01}(\bar{\sigma}) = 6^{-\frac{1}{2}}\left(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha\right)$$
$$\Theta^{3}_{\frac{1}{2}02}(\bar{\sigma}) = 2^{-\frac{1}{2}}\left(\alpha\beta\alpha - \beta\alpha\alpha\right) \qquad \text{(II.2)}$$

The spatial part is the product,

$$\chi(\bar{r}) = \prod_{i=1}^{3} \phi_i(\bar{r}_i) + \prod_{i=1}^{3} \phi_i'(\bar{r}_i) \qquad \text{(II.3)}$$

where the ϕ_i are of the form,

$$\phi_i(\delta,\alpha; n,m,\nu) = \exp[-(\delta_i\xi_i + \alpha_i\eta_i + i\nu_i\phi_i)]\, \xi_i^{n_i}\, \eta_i^{m_i} \left[(\xi_i^2-1)(1-\eta_i^2)\right]^{\frac{|\nu_i|}{2}} \qquad \text{(II.4)}$$

and the ϕ_i' are,

$$(-1)^{m_i + |\nu_i|}\ \phi_i(\delta, -\alpha; n,m,\nu) \qquad \text{(II.5)}$$

ξ, η and ϕ being the standard two-center elliptical coordinates. The δ_i, α_i are variable within the computer program used, but n,m,ν are input parameters and therefore fixed throughout the problem. The configuration chosen was:

$$\phi_1(\delta_1,\alpha_1; 0,0,0)\, \phi_2(\delta_2,\alpha_2; 0,0,1)\, \phi_3(\delta_3,\alpha_3; 2,0,-1) + \phi_1'\phi_2'\phi_3' \qquad \text{(II.6)}$$

It is convenient to denote these in terms of the ν_i, since none of the n,m,ν change and all $m_i = 0$. Thus,

$$\chi(\bar{r}) = \phi_0\phi_1\phi_{-1} + \phi_0'\phi_1'\phi_{-1}' \qquad \text{(II.7)}$$

Since $\Sigma m_i = 0$ and $\Sigma|\nu_i| = 2$, there is no sign change between the products, and gerade symmetry is ensured. Also, $\Sigma\nu_i = 0$, so the three electron product is a Σ state.

Note that if the outer electron is removed (placed in the continuum),

$$\chi(\bar{r}) = [\phi_0\phi_1 + \phi_0'\phi_1']\,\phi(3) \qquad \text{(II.8)}$$

is obtained, which is a Π state ($\Sigma\nu \neq 0$) with ungerade symmetry since the ϕ_1'

introduces a - sign between the products. Thus it has been spatially ensured that the 1 configuration variation function cannot vary itself to H_2 $^1\Sigma_g$ + e by varying δ_{-1} to a very small number which has the effect of ejecting the outer electron into the continuum.

Looking at the spin portion, it is also noted that $\Theta^{3}_{\frac{1}{2}02}$ can "lose" an electron to become,

$$\Theta^{2}_{001}\,\alpha(3) = 2^{-\frac{1}{2}}\left[(\alpha\beta-\beta\alpha)\right]\alpha(3) \qquad \text{(II.9)}$$

which is the spin eigenfunction for a two electron singlet.

The one-configuration variation function is now constrained in such a manner that it cannot eject the outer electron and become anything but H_2 $^1\Pi_u$ + e, and the resonant wave packet is suitably localized by these constraints.

III. Calculations and Results

In order to obtain a potential curve and the spectroscopic constants for comparison with those reported by experiment,[4] it was planned to calculate five energy values at nuclear radii corresponding to scaled roots of the fifth order Chebyschev polynomial $T_5(x)$, where $x = R - R_e/.34026$, which gives separations of ± .2000 and ± .3236 au. about R_e, and fit these to Chebyschev polynomials T_0 through T_4.[12] The spectroscopic constants could then be calculated by the method of Dunham.[13]

Preliminary calculations with a trial function of the type $1\sigma(1\pi)^2$ yielded an equilibrium radius of 1.9196 au., and the final full variation of the δ and α parameters was done about this R_e. Upon fitting to the Chebyschev polynomials and minimizing $E(R)$ with respect to R, R_e was found to be 1.949 au. instead of 1.9196, so Dunham's method, based on a polynomial in $(R - R_e)/R_e$, becomes excessively tedious. Therefore, the polynomial in x was converted to a polynomial in R and the vibration-rotation constants calculated by the method used by Fraga and Ransil in ref. 14.

To note the effect of greater interatomic distances three other R values were used. Table I gives the potential curve and parameters of the wave function.

Table II is a comparison of the calculated spectroscopic constants with those reported in the scattering experiment.

It is also of interest to note in Table III that as R increases, the potential curve approaches the curve of the $^1\Pi_u$ state of H_2.[15] This can be explained by inspection of the parameters of the three electrons. At $R = 10.0$ au. there is essentially a 1s hydrogen atom and a 1p hydrogen atom widely separated, with an electron in between. In H_2 $^1\Pi_u$ at this internuclear distance, the expected configuration is a pair of hydrogen atoms, one in the 1s state and one in the 1p state.

This seems to indicate that H_2^- cannot be formed by collision of H and H^-, but only by collision of H_2 with an electron. Also, the proposed mechanism for formation of H and H^- by dissociation of H_2^- may have another step,

$$H_2 + e \longrightarrow (H_2^-) \longrightarrow (H_{1s} + H_{2p} + e) \longrightarrow H + H^-$$

where the H_{2p} may recapture the electron of the H_2^- or capture another of the electrons in the experimental system.

IV. Conclusions

The potential curve and electronic wave function for the resonant $^2\Sigma_g$ state of H_2^- have been calculated by treating a one-configuration trial function as if it were a real variation function which could be minimized to a real discrete eigenvalue. An average energy very near to the experimentally observed energy was obtained, however, since this is a state in the continuum there is no rigorous minimum principle, and the calculated average energy may be above or below the actual energy of the system.

There is no doubt that if the configuration determining parameters n, m, and v were also allowed to vary, the final result would have been the one configuration approximation to the ground state energy of the hydrogen molecule.

Excellent agreement with experimental spectroscopic constants has been obtained, which substantiates the statement that this is a resonance with a lifetime long enough to be observable, and the use of physical intuition to pick a restricted variation function which simulates an electron scattering off a deep, narrow potential well formed by an excited state of H_2.

The method of finding the longest-lived wave packet in the continuum by a restricted variation method coupled with good physical guesses may have considerable application in other problems.

It is the intuitive feeling of the authors that all resonant states will be able to be treated by this approximate method, because if they have a long enough lifetime to be observed, they are probably weakly correlated, in the sense described above and therefore amenable to approximate variation treatment. This may not be a necessary condition, but it is certainly a sufficient one. The lack of rigor prescribes great care in any application.

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Table I[a]

Wave Function and Potential Curve

R (au)	-E (au)	δ	α	R (au)	-E (au)	δ	α
1.596	.74336	1.115	.765	2.2432	.74488	1.420	1.020
		.445	-.17			.635	-.255
		.100	0.0			.105	0.0
1.7196	.74848	1.175	.810	3.000	.71513	1.75	1.34
		.485	-.185			.82	-.38
		.105	0.0			.11	0.0
1.9196	.75064	1.270	.890	7.000	.63377	3.53	3.39
		.550	-.210			1.78	-1.66
		.105	0.0			.11	0.0
2.1196	.74804	1.365	.970	10.000	.62929	5.01	4.96
		.600	-.240			2.51	-2.50
		.105	0.0			.11	0.0
				15.00[b]	.61332	6.24	6.21
						3.76	-3.76
						.10	0.0

a. Throughout this table, the electron parameters are listed in the order $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 2 & 0 & -1 \end{pmatrix}$ so that the inner electron is first, and the outer resonant electron is last.

b. This point was not completely varied, but a definite continuation of the trend to $H_{1s} + H_{1p} + e^-$ is exhibited.

Table II

Comparison of Spectroscopic Constants

	calculated	experimental
E	$-.75148$ au	$-.738$ au
R_e	1.949 au	
ω_e	.30 ev	.31 ev
$\omega_e x_e$	.042 ev	$\sim .01$ ev
B_e	.0039 ev	
α_e	3×10^{-4} ev	
D_e	5.36 ev	

[illegible]

[illegible]

[illegible]		
[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]

Table III

Comparison with H_2 $^1\Pi_u$ Potential Curve

R (au)	-E H_2C $^1\Pi_u$[a]	-E H_2^- $^2\Sigma_g$	ΔE
1.9	.71422	.75057	.03635
2.0	.71418	.74800	.03382
2.25	.71006	.74481	.03475
3.0	.68445	.71513	.03068
7.0	.62478	.63377	.00899
10.0	.62448	.62929	.00481

a. From ref. (12)

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